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AN EXPLICIT MODEL FOR THE NMR COUPLING CONSTANT OF THE HYDROGEN MOLECULE AND THE BREAKDOWN OF INDO–FPT

PATRICK REDINGTON, DENNIS CALDWELL,* AND HENRY EYRING

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112, USA

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Abstract—We have previously obtained explicit equations, which are based on the ideas of finite perturbation theory (FPT), for calculating NMR proton–proton coupling constants. Using this model and the INDO formalism, a simple closed-form expression for the coupling constant of the hydrogen molecule is developed. This expression has several unique features: it shows that the convergence criteria for the iterative calculation is $|x| < 1$, where $x = \gamma_{HH}/\Delta\epsilon$; and it allows the H_2 coupling constant to be expressed directly in terms of the semiempirical parameters, showing specifically how each parameter affects the coupling constant. In this way the formalism of semiempirical SCF theory lends itself to the construction of a model for coupling constants which is not purely numerical in nature. An INDO–FPT calculation is developed for the hydrogen molecule. As long as parameters are chosen for which $|x| < 1$ the unrestricted Hartree-Fock (UHF) portion of the FPT calculation behaves properly and the explicit and FPT predictions for the coupling constant agree. When $|x| > 1$, the UHF calculation breaks down, the extremum corresponding to symmetrical molecular orbitals no longer being the minimum.

I. INTRODUCTION TO FINITE PERTURBATION THEORY

For protons the contact portion of the magnetic Hamiltonian

$$\hat{H}_A' = \frac{16\pi}{3}\beta\sum_k \delta(r_{kA})\, S_{kz} \tag{1}$$

is considered to be the most important, accounting for the largest part of the coupling.

Considering the contact Hamiltonian only, Pople, McIver, and Ostland [1] showed that the coupling constant is given by

$$J_{AB} = \frac{\hbar}{2\pi}\frac{8\pi\beta}{3}\gamma_A\gamma_B\sum_{rs}\int \phi_r\,\delta(\mathbf{r}_A)\,\phi_s\,d\tau\left[\frac{\partial}{\partial\mu_\beta}\rho^{\text{spin}}(\mu_\beta)\right]_{\mu_B=0}, \tag{2}$$

where β is the Bohr magneton, γ is the nuclear magnetogyric ratio, ϕ are the atomic orbitals, and μ is the magnetic moment of a nucleus.

* Present address: Hercules, Inc., Aerospace Division, Bacchus Works, P.O. Box 98, Magna, Utah 84044, USA.

Finite perturbation theory (FPT) [1,2] treats NMR coupling constants by calculating the derivative in Eq. (2). This is accomplished using an unrestricted Hartree-Fock (UHF) calculation, where the α and β electrons have distinct spatial orbitals. The net spin density is then the difference between the α and β density matrices:

$$\boldsymbol{\rho}^{\text{spin}} = \mathbf{P}^{\alpha} - \mathbf{P}^{\beta}. \tag{3}$$

In this formalism the Fock matrix elements are

$$\overset{\alpha}{F}{}^{\beta}_{mn} = H_{mn} \pm H'_{mn} + \sum_{rs} \left(P_{rs} \langle mn|rs\rangle - \overset{\alpha}{P}{}^{\beta}_{rs} \langle mr|ns\rangle \right) \tag{4}$$

where H_{mn} is the core Hamiltonian, H'_{mn} is the modification due to the perturbation, and $P_{mn} = P^{\alpha}_{mn} + P^{\beta}_{mn}$.

FPT is most commonly applied in the INDO [2] formalism, in which case H'_{mn} is zero unless $m=n=1s$ valence orbital on atom B. Therefore

$$H'_{BB} = h_B = \frac{8\pi}{3} \beta\mu_B S_B^2(0) \tag{5}$$

and

$$\begin{aligned} \int \phi_r \delta(\mathbf{r}_B) \phi_s \, d\tau = S_B^2(0), \text{ if } \phi_r = \phi_s = 1s \text{ valence} \\ \text{orbital of atom } B \\ = 0 \qquad \text{otherwise.} \end{aligned} \tag{6}$$

Thus, implementation of the perturbation merely involves addition and subtraction of h_B to the standard expressions for F^{α}_{mn} and F^{β}_{mn}, respectively. In practice, the calculation involves choosing a value for h_B (0.001 is commonly used [1]) and the derivative is evaluated using finite differences:

$$\frac{\partial \rho^{(\text{spin})}_{S_A,S_A}}{\partial \mu_B(\mu_B=0)} \propto \frac{\rho^{(\text{spin})}_{S_A,S_A}(h_B)}{h_B} \tag{7}$$

Even though it may lead to no direct improvement in numerical results, there is some considerable advantage in a formulation of the method which explicitly displays the results as a function of the molecular parameters and in turn relates, so far as possible, to experimental quantities. The explicit form one obtains [3,4] is

$$J_{AB} = 4 \frac{\hbar}{2\pi} \left(\frac{8\pi\beta}{3} \right)^2 \gamma_A \gamma_B S_A^2(0) \, S_B^2(0) \sum_{ai} \frac{h^{A(\infty)}_{ai} \, h^{B(\infty)}_{ai}}{\Delta ai}, \tag{8}$$

where

$$\overset{(n+1)}{h}{}^{A}_{ai} = \overset{(0)}{h}{}^{A}_{ai} - \sum_{bj} \frac{h^{A(n)}_{bj}}{\Delta bj} \left(\langle ab|ij\rangle + \langle aj|ib\rangle \right) \tag{9}$$

$$\overset{(0)}{h}{}^{A}_{ai} = C_{Aa} C_{Ai} \, . \tag{10}$$

The indices a and b are sums over the occupied molecular orbitals, while i and j are over the virtual molecular orbitals, and

$$\Delta_{ai} = \epsilon_a - \epsilon_i \,. \tag{11}$$

II. CLOSED FORM FOR J_{AB} of H_2.

Using the explicit form to evaluate the coupling constant of the hydrogen molecule provides results which are particularly illuminating. In the semiempirical formalism the hydrogen molecule has one occupied orbital a and one virtual orbital i. This allows Eq. (9) to be written out in the form,

$$\begin{aligned}
&h_{ai}^{A(0)} = C_{Aa}C_{Ai} \\
&h_{ai}^{A(1)} = h_{ai}^{A(0)} - h_{ai}^{A(0)}\, x \\
&h_{ai}^{A(2)} = h_{ai}^{A(0)} - h_{ai}^{A(0)}\, x + h_{ai}^{A(0)}\, x^2 \\
&\quad\vdots \\
&h_{ai}^{A(\infty)} = h_{ai}^{A(0)}\,(1 - x + x^2 - x^3 + x^4 - \cdots)
\end{aligned} \tag{12}$$

with

$$x = \frac{\langle aa|ii\rangle + \langle ai|ai\rangle}{\Delta\epsilon} = \frac{\gamma_{HH}}{\Delta\epsilon} \,. \tag{13}$$

The infinite sum in Eq. (12) will converge as long as $|x| < 1$ in which case

$$h_{ai}^{A(\infty)} = h_{ai}^{A(0)} \frac{1}{1+x} \,. \tag{14}$$

Using $S_A^2(0) = 0.3724$ [1] and evaluating the numerical constant gives

$$J_{AB} = -105.04 \frac{1}{\Delta\epsilon + \gamma_{HH}} \text{ Hz}, \tag{15}$$

where $\Delta\epsilon$ is in atomic units.

III. PARAMETERIZATION AND J_{AB}

At the experimental internuclear distance of 1.4 Å an INDO calculation gives $\Delta\epsilon = -0.5742$ and $\gamma_{HH} = 0.75$, resulting in $J_{AB} = -597.5$ Hz, while the experimental value is +280 Hz. With these parameters, not even the predicted sign is correct. The reason for this is clear when the value of x is checked, i.e., $|x| = 1.31$.

Combining the parameterization philosophies of CNDO/1 and INDO leads to a set of parameters which is more satisfactory. INDO uses the theoretical value for γ_{HH}, which is too large. A semiempirical choice, which is better, can be made. The INDO prescription is

$$-\tfrac{1}{2}(I+A)_s = U_{ss} + \tfrac{1}{2}\gamma_{HH}\,, \tag{16}$$

where I is the ionization potential, A the electron affinity, and U_{ss} the core integral. In INDO, U_{ss} is determined by the theoretical value of γ_{HH}. In CNDO/1 the relation

$$U_{ss} = -I_s \tag{17}$$

is used. Combining Eqs. (16) and (17) allows a semiempirical choice for γ_{HH}, namely

$$\gamma_{HH} = (I-A)_s. \tag{18}$$

With this relation and the trace relationship, one may obtain

$$\Delta\epsilon + \gamma_{HH} = 2(\epsilon+I_H)\,. \tag{19}$$

If Koopmans' theorem is used, then

$$J_{AB} = 105.04\,\frac{1}{2(I(H_2) - I(H))}\ \text{Hz}\,. \tag{20}$$

The experimental values $I(H_2) = 15.42$ eV [5] and $I(H) = 13.527$ eV [6] give $J_{AB} = 754.9$ Hz which is at least the correct sign. Certainly this approximation of $2(I(H_2) - I(H)) = 3.79$ eV for the lowest triplet energy is poor, the experimental value being 11.752 eV [7]. When the correct triplet energy is used, the more reasonable value, $J_{AB} = 243.2$ Hz, is obtained.

These results show the model is on the right track but parameters are a problem. An analysis of the UHF–FPT calculation leads to an understanding of the failure of the standard INDO parameters.

IV. DEVELOPMENT OF THE UHF–FPT CALCULATION

This problem may be written as a function of one variable where the LCAO coefficients are given by

$$\mathbf{C}^{\alpha} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \qquad \mathbf{C}^{\beta} = \begin{pmatrix} \sin\theta & \cos\theta \\ \cos\theta & -\sin\theta \end{pmatrix} \tag{21}$$

allowing the density matrix elements to be written as

	α	β	$\alpha+\beta$
P_{AA}	$\cos^2\theta$	$\sin^2\theta$	1
P_{AB}	$\cos\theta\sin\theta$	$\cos\theta\sin\theta$	$2\cos\theta\sin\theta$
P_{BB}	$\sin^2\theta$	$\cos^2\theta$	1

(22)

In the INDO approximation this problem will have three types of nonzero integrals:

$$\begin{aligned} \langle AA|AA\rangle &= \gamma_{AA} = \gamma_{HH} \\ \langle BB|BB\rangle &= \gamma_{AA} \\ \langle AA|BB\rangle &= \gamma_{AB} . \end{aligned} \tag{23}$$

The Fock matrix elements are

$$\begin{aligned} F^{\alpha}_{AA} &= H_{AA} + \gamma_{AA} \sin^2\theta + \gamma_{AB} \\ F^{\alpha}_{AB} &= H_{AB} - \gamma_{AB} \cos\theta \sin\theta \\ F^{\alpha}_{BB} &= H_{AA} + \gamma_{AA} \cos^2\theta + \gamma_{AB} + h_B \end{aligned} \tag{24}$$

$$\begin{aligned} F^{\beta}_{AA} &= H_{AA} + \gamma_{AA} \cos^2\theta + \gamma_{AB} \\ F^{\beta}_{AB} &= H_{AB} - \gamma_{AB} \cos\theta \sin\theta \\ F^{\beta}_{BB} &= H_{AA} + \gamma_{AA} \sin^2\theta + \gamma_{AB} - h_B \end{aligned} \tag{25}$$

and the general expression for the electronic energy

$$\begin{aligned} E = &\sum_{pq} (P^{\alpha}_{pq} F^{\alpha}_{pq} + P^{\beta}_{pq} F^{\beta}_{pq}) \\ &- \sum_{pq} \sum_{rs} [P_{pq} P_{rs} \langle pq|rs\rangle - (P^{\alpha}_{pq} P^{\alpha}_{rs} + P^{\beta}_{pq} P^{\beta}_{rs}) \langle pr|qs\rangle] , \end{aligned} \tag{26}$$

simplifies to

$$E = A \sin^2\phi + B \sin\phi + C - h_B \cos\phi , \tag{27}$$

where

$$\begin{aligned} A &= (\gamma_{AA} - \gamma_{AB}) \\ B &= 2H_{AB} \\ C &= 2H_{AA} + \gamma_{AB} \\ \phi &= 2\theta \end{aligned} \tag{28}$$

In order to find the minimum value for E one solves

$$\frac{\partial E}{\partial \phi} = 0 = A \sin 2\phi + B \cos\phi + h_B \sin\phi = 0 . \tag{29}$$

A commonly used technique is the Newton–Raphson method [8]. There is no guarantee that the Newton–Raphson will converge. When it does converge ϕ will be a solution to Eq. (29), but it may be a maximum or a minimum. Evaluation of the second derivative

will indicate whether or not a solution is a maximum or a minimum. The iterative form the Newton–Raphson iteration takes is

$$\phi_{n+1} = \phi_n - \left\{ \frac{\phi_n - \cos^{-1}\left(- \dfrac{h_B \sin\phi_n - A \sin 2\phi_n}{B} \right)}{1 + \dfrac{h_B \cos\phi_n + 2A \cos\phi_n}{\sqrt{1 - \dfrac{(-h_B \sin\phi_n - A \sin 2\phi_n)^2}{B}}}} \right\} \tag{30}$$

If the Newton–Raphson fails to converge or finds a maximum, a direct search using the Fibonacci algorithm [9] may be used to locate $\phi_{\min}$.

Once $\phi_{\min}$ has been determined, the coupling constant may be evaluated. The FPT derivative expression is

$$J^F_{AB} = 105.04 \frac{\cos\phi}{h_B} \text{ Hz.} \tag{31}$$

Now that ϕ is allowed to take on values other than 90° the expression for x must be written in its complete form. If we define

$$X' = \sin^2\phi \frac{\gamma_{HH}}{\Delta\epsilon}, \tag{32}$$

the explicit expression for the coupling constant is

$$J^E_{AB} = -105.04 \frac{1}{\Delta\epsilon + \gamma_{AA} \sin^2\phi} \text{ Hz}. \tag{33}$$

Since the numerical constants are the same except for the sign, it is convenient to define a "reduced" coupling constant

$$J^F_R = \frac{\cos\phi}{h_B} \tag{34}$$

$$J^E_R = \frac{-1}{\Delta\epsilon + \gamma_{AA} \sin^2\phi} \tag{35}$$

The semiempirical parameters in this calculation are H_{AA}, H_{AB}, γ_{AA}, and γ_{AB}. x, x', and J may be expressed in terms of these parameters and the variable ϕ:

$$\Delta\epsilon = B - \gamma_{AB} \sin\phi \tag{36}$$

$$x = \frac{\gamma_{AA}}{B - \gamma_{AB} \sin\phi} \tag{37}$$

$$x' = x \sin^2\phi \tag{38}$$

$$J^E_R = \frac{-1}{B - \gamma_{AB} \sin\phi + \gamma_{AA} \sin^2\phi}. \tag{39}$$

It is clear from Eqs. (29), (37), (38), and (39) that H_{AA} has no effect on J_{AB}, x, x', or ϕ and thus serves only to adjust the value of E.

Table 1.

Parameter	Min	Average	Max
H_{AB}	−0.3617	−0.2330	−0.1042
γ_{AA}	0.4325	0.5913	0.7500
γ_{AB}	0.2016	0.2838	0.3659

Systematically varying H_{AB}, γ_{AA}, and γ_{AB} will serve a twofold purpose: it will show whether this method is capable of predicting the experimental value of J_{AB} and give some indication of what occurs whenever $|x| > 1$. Estimates of "reasonable" ranges over which to vary these parameters can be made using various semiempirical relationships. Our estimates are given in Table 1. The experimental value for the coupling constant requires a set of parameters which gives $J_R^F = 2.666$ and $J_R^E = -2.666$. From the possible combinations the two best sets of parameters are given in Table 2. This provides a good estimate for J_{AB} within this "reasonable" range of parameters.

Table 2.

H_{AB}	γ_{AA}	γ_{AB}	$\lvert x\rvert$	$\phi_{\min}$	J_R^F	J_R^E
−0.2330	0.4325	0.3659	0.5199	89.86	2.504	−2.504
−0.3617	0.7500	0.3659	0.6885	89.83	2.947	−2.947

The other parameter, H_{AA}, may be related to the occupied orbital energy via Koopmans' theorem

$$\epsilon = H_{AA} = \tfrac{1}{2}(\gamma_{AA}+\gamma_{AB}) + H_{AB} = -I(H_2) \tag{40}$$

or to the total electronic energy

$$E = \tfrac{1}{4}(\gamma_{AA}-\gamma_{AB}) + 2H_{AA} + 2H_{AB} + \gamma_{AB}. \tag{41}$$

V. IMPORTANCE OF $|x|$.

With the proper choice of parameters this model behaves well and is capable of making predictions which are in good agreement with experiment. A simple test for determining th acceptability of the parameters H_{AB}, γ_{AA}, and γ_{AB}, namely $|x|$ arose naturally in the development of the explicit expression for the coupling constant. As long as $|x| < 1$, J_R^F and J_R^E are in agreement. This is shown graphically in Fig. 1, where $\| J_R^F| - |J_R^E \|$ vs $|x|$ is plotted. The point immediately to the left of 1.0 is $x = 0.902$ for which $F(x) = 100.51$. The reasons for this behavior will be clear from the following analysis.

The magnitude of x can be used as a general test, indicating the success or failure of the UHF–FPT calculation. Its effect on the FPT energy map is shown in Fig. 2 where E vs ϕ is plotted for four different values of $|x|$ with a constant $H_{AA} = -1.0046$. The summary is shown in Table 3.

At this point we should note the effect of h_B on the calculation. This was studied by choosing a set of parameters for which $|x| < 1$ and then varying h_B between 10^{-5} and 1.0

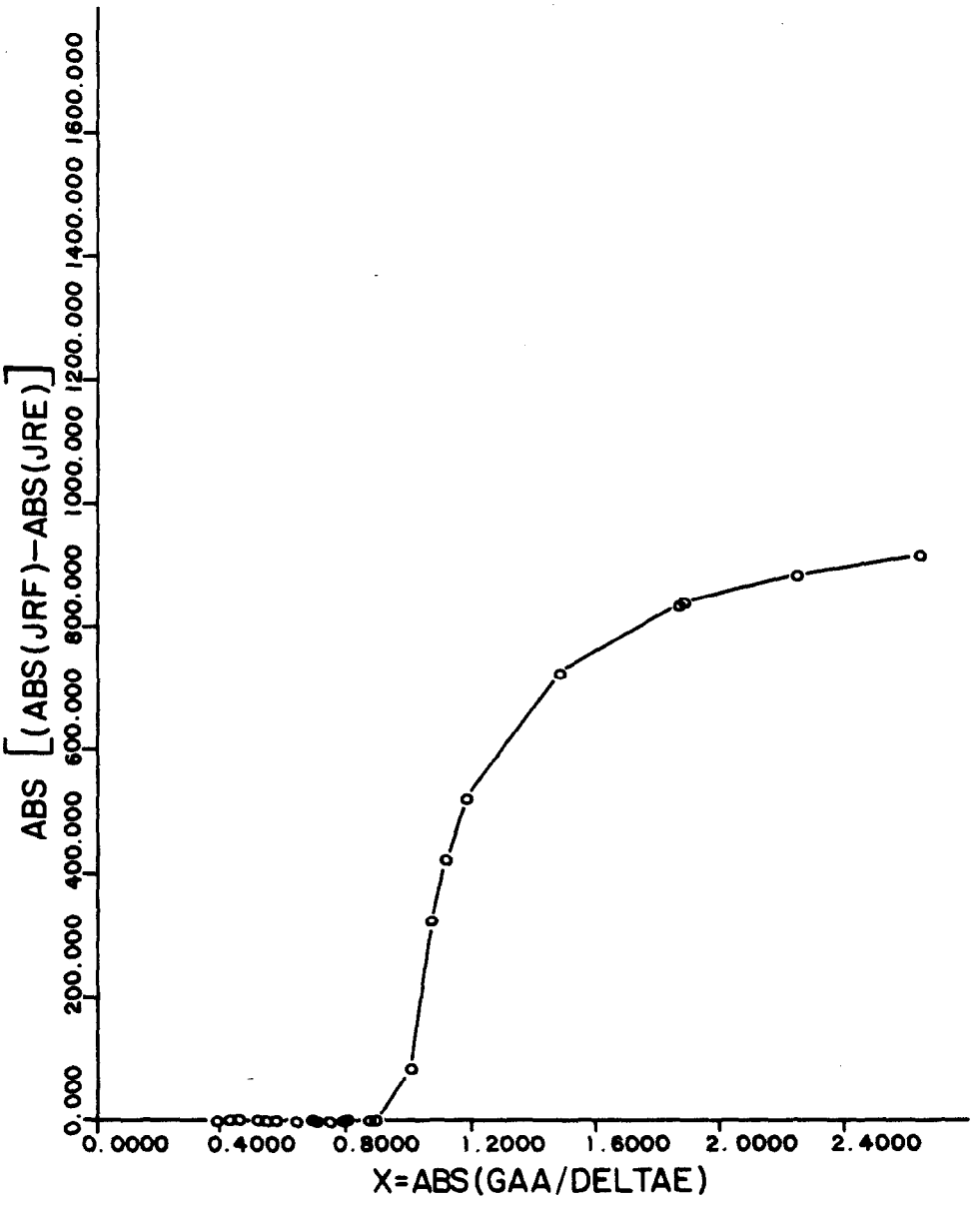

Fig. 1.

in powers of 10. E_{min}, J_R^E, and J_R^E were all consistent for the range 10^{-5} to 10^{-3}. At 10^{-2} the solutions began to break down and for all larger values were completely distorted. The optimum value for h_B is found to be 10^{-3} [1]. This value is small enough so as not to distort the solution yet large enough to help minimize numerical error. All the calculations reported in this work used $h_B = 10^{-3}$.

When $h_B = 0$, Eq. (29) can be solved explicitly. Then an analysis of the UHF case is much simpler. Since h_B is very small, the differences between the UHF and FPT results are minimal, as can be seen in the data for Fig. 2. The picture resulting from the simple analysis may also be applied to the FPT case.

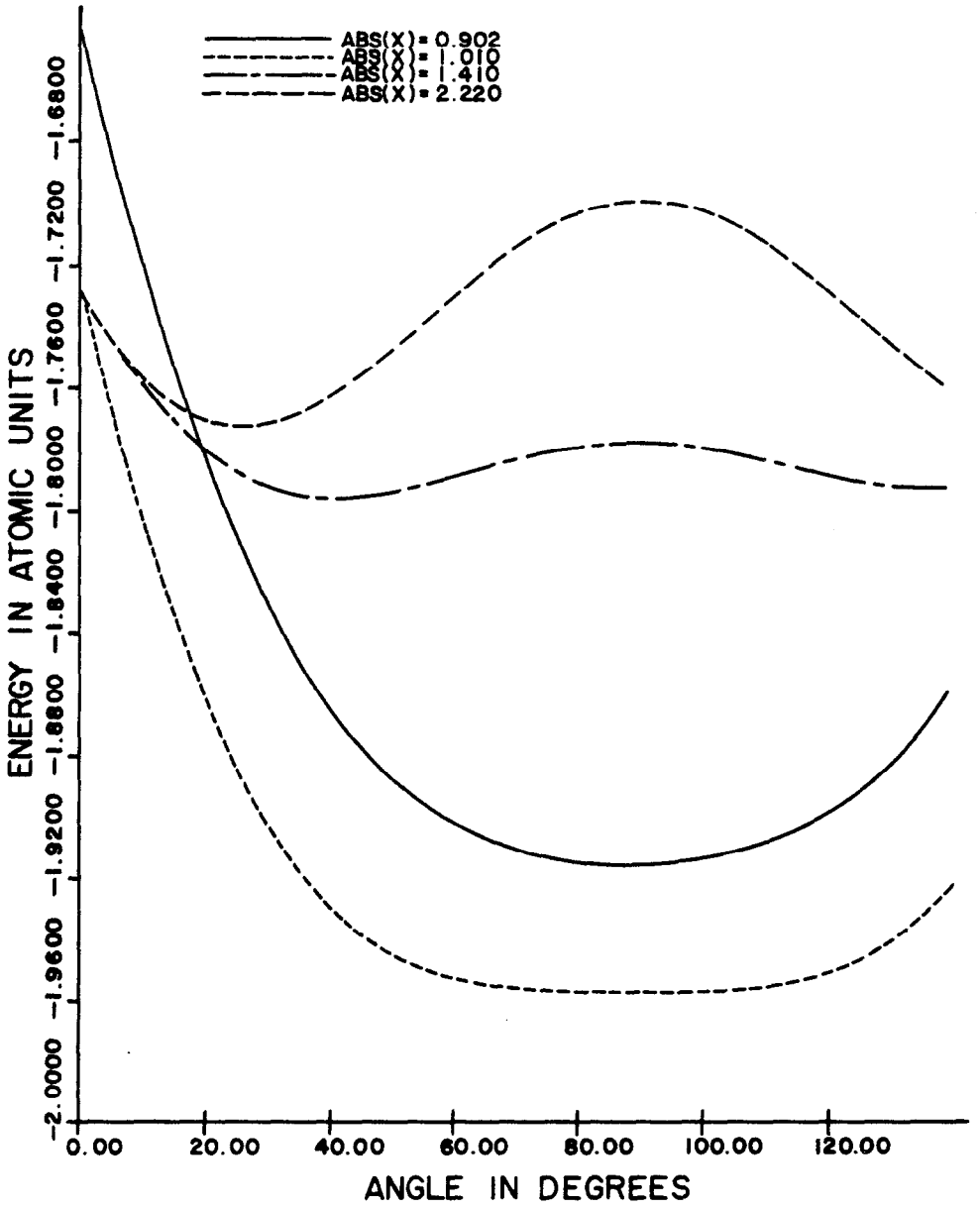

Fig. 2.

Table 3. Summary of data for the plots in Fig. 2.

H_{AB}	γ_{AA}	γ_{AB}	$\lvert x\rvert$	ϕ_{min}^{FPT}	ϕ_{min}^{UHF}
−0.2330	0.7500	0.3659	0.9020	89.30	90.00
−0.2330	0.7500	0.2838	1.010	80.61	88.32
−0.1042	0.5913	0.2838	1.410	42.90	42.67
−0.1042	0.7500	0.2838	2.220	27.00	26.55

Setting $h_B = 0$ reduces $(\partial E/\partial\phi)$ to

$$\cos\phi(2A\ \sin\phi + B) = 0\ , \tag{42}$$

which has two possible solutions

$$\phi = 90° \text{ or } \phi = \sin^{-1}\frac{B}{2A}\ . \tag{43}$$

It turns out that $|x|$ may be used to indicate which of these solutions are valid. If $-B/2A < 1$, then $\phi = 90°$ is the only possible solution. The expression for $|x|$ is

$$|x| = \left|\frac{\gamma}{B-\gamma_{AB}}\right| = \frac{|\gamma|}{B-\gamma_{AB}} < \left|\frac{\gamma}{B-\gamma_{AB}}\right| = 1\ , \tag{44}$$

because $-B > 2A = (\gamma_{AA} - \gamma_{AB})$. A second solution would require $-B < 2A$. In this case the expression for $|x|$ is

$$|x| = \frac{|2A\gamma_{AA}|}{|B(2A+\gamma_{AB})|} > \frac{|(-B)\gamma_{AA}|}{|B\gamma_{AA}|} = 1\ . \tag{45}$$

Accordingly whenever $|x| > 1$ there are two solutions:

$$\phi = 90° \text{ and } \phi = \sin^{-1}\left(\frac{B}{2A}\right)\ . \tag{46}$$

Evaluation of $(\partial^2 E/\partial\phi^2)$ provides a means to determine whether a solution is a maximum or a minimum. The expression for the second derivative is

$$\frac{\partial^2 \mathrm{E}}{\partial\phi^2} = 2A\ \cos 2\phi - B\ \sin\phi\ . \tag{47}$$

Whenever $|x| < 1$, the only solution is $\phi = 90°$ which gives

$$\frac{\partial^2 E}{\partial\phi^2} = -2A - B > 0\ . \tag{48}$$

When $|x| > 1$, the inequalities are reversed making the solution at 90° a local maximum. The other solution is $\phi = \sin^{-1}(B/2A)$ in which case

$$\frac{\partial^2 E}{\partial\phi^2} = \frac{(2A+B)\,(2A-B)}{2A} > 0\ , \tag{49}$$

so this solution will be the minimum.

The standard INDO parameters are $H_{AA} = -1.0046$, $H_{AB} = -0.1042$, $\gamma_{AA} = 0.7500$, and $\gamma_{BB} = 0.3659$ giving a UHF minimum at 32.8586° ($E = -1.6998$) and a local maximum at $\phi = 90°$ ($E = -1.6597$, the exact value that the INDO computer program gives). At

the minimum the coefficients are

$$\mathbf{C}^{\alpha} = \begin{pmatrix} 0.9592 & 0.2828 \\ 0.2828 & -0.9592 \end{pmatrix}, \qquad \mathbf{C}^{\beta} = \begin{pmatrix} 0.2828 & 0.9592 \\ 0.9592 & -0.2828 \end{pmatrix} \tag{50}$$

and the Fock matrix elements are

$$\mathbf{F}^{\alpha} = \begin{pmatrix} -0.5787 & -0.2035 \\ -0.2035 & 0.0513 \end{pmatrix}, \qquad \mathbf{F}^{\beta} = \begin{pmatrix} 0.0513 & -0.2035 \\ -0.2035 & -0.5787 \end{pmatrix} \tag{51}$$

giving a result which lacks the proper symmetry.

The UHF–INDO computer program [2] will always give the symmetric result because the initial approximation to the Fock matrix sets $F_{AA}^{\alpha\beta} = F_{BB}^{\alpha\beta}$. This is analogous to using $\phi = 90°$ as the starting point for the Newton–Raphson iteration.

Another peculiarity of this breakdown occurs in the coupling constant calculation. As just pointed out the regular FPT calculation will always generate a solution which is close to 90°. When J_R^F and J_R^E are computed using this solution they are in good agreement. At a solution point, Eq. (29) is valid so that

$$h_B = -\frac{A \sin 2\phi + B \cos\phi}{\sin\phi} . \tag{52}$$

Substituting this result into the expression for J_R^F gives

$$J_R^F = \frac{-\sin\phi}{B - \gamma_{AB} \sin\phi + \gamma_{AA} \sin\phi} . \tag{53}$$

When $\phi = 90°$, this is identical to the expression for J_R^E [Eq. (33)]. Thus, when ϕ is close to 90° the agreement between J_R^F and J_R^E will be very good.

The explicit expression will always be valid when evaluated at $\phi_{\min}$. Since $x' = x(\sin^2\phi)$ when ϕ is close to 90° (i.e., $|x| < 1$) then $|x'| < 1$. When $|x| > 1$, $\sin\phi = (-B/2A)$, so that

$$x' = -\frac{B}{2A} \leq 1 . \tag{54}$$

It would take a particularly bad choice of parameters for the inequality not to hold.

CONCLUSION

In its normal matrix diagonalization form the UHF–FPT treatment of the hydrogen molecule provides only one point on the energy map and the solution at that point reflects the proper symmetry making a breakdown impossible to detect. The absolute value of x proved to be a convenient indicator of the breakdown. Although there is no direct analog of x for larger molecules, the iterative procedure will signal a breakdown by diverging [3].

Computationally this calculation is less efficient than FPT [10,11] because evaluation of the $\langle ab|ij\rangle$ is a time consuming process, but it does have the redeeming features of

signalling bad parameters and of giving insight into the workings of an otherwise numerically oriented analysis.

A very interesting case is the heteronuclear molecule X–Y, which can serve as the basis for a model for the contact coupling between different types of directly bonded nuclei. Due to the lack of symmetry, there are two variables in this problem requiring a coupled solution which does not have quite the simple form of the hydrogen molecule [12]. Work on this problem is continuing.

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